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13. ABSTRACT (Maximum 200 words)

Using theoretical models and computer simulations, we determined guidelines for promoting the uniform dispersion (exfoliation) of clay sheets in polymer melts. In addition, we determined how the coupling between phase separation and wetting interactions in polymeric composites effects the structural evolution and phase behavior of the material. We also developed a mean field theory for mixtures of soft, flexible chains and hard spheres. Applied to diblock/nanoparticle mixtures, and theory predicts new ordered phase, where particles and diblocks self-assemble into spatially periodic structures. The method can be applied to other copolymer/particle mixtures and used to design novel composite architectures.

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Enclosure 3

Final Progress Report

(1) Statement of the Problem Studied

Our aim was to determine the phase behavior and dynamics of polymer blends and composites. In particular, we used theoretical models and computer simulations to establish guidelines for promoting the uniform dispersion (exfoliation) of clay sheets in polymer melts. In addition, our goal was to determine how the coupling between phase separation and wetting interactions in polymeric composites effects the structural evolution and phase behavior of the material.

(2) Summary of Most Important Results

We combined a density functional theory (DFT) with a self-consistent field model (SCF) to calculate the phase behavior of thin, oblate colloidal particles that are coated with surfactants and dispersed in a polymer melt. These coated particles represent organically modified clay sheets. By integrating the two methods, we can investigate the effect of the surfactants' characteristics (grafting density and length) and the polymer-surfactant interaction energy on the polymer-clay phase diagram. Depending on the values of these critical parameters and the clay volume fraction, the system can be in an isotropic or nematic phase (which corresponds to an exfoliated composite). The system can also form a smectic, crystal, columnar, or "house-of-cards" plastic solid, as well as a two-phase (immiscible) mixture. Using this model, we isolated conditions that lead to the stabilization of the homogeneous, exfoliated phases (the isotropic and nematic regions) and to the narrowing of the immiscible two-phase regions.

We developed a computer simulation for the dynamic behavior of a phase-separating binary mixture that contains mobile, solid particles. The system models "filled polymers", which contain not only a blend of different macromolecules, but also solid fillers. We focused on the case where one of the components preferentially wets the surface of the particles. By combining a mesoscopic, coarse-grained description of the fluids with a discrete model for the particles, we show that the addition of hard particles significantly changes both the speed and the morphology of the phase separation. To probe the late-stage properties of the system, we also developed a mean-field rate-equation model for the mixture. The results indicate that the phase separation is arrested in the late stage; the "steady-state" domain size depends strongly on both the particle diffusion constant and the particle concentration. To obtain insight into the effects of processing on the properties of such composites, we also investigated the behavior of the binary fluid/particle mixture under shear. For sufficiently large particle densities, we find that the anisotropic growth caused by the imposed shear is destroyed by the randomly moving particles, and the domains are isotropic in shape even for large shear strains. Finally, we applied our models to mixtures of diblock copolymers and fillers. Overall, our findings reveal how the solid additives can be used to tailor the morphology of the complex mixture, and thereby control the macroscopic properties (such as mechanical integrity) of the composite.

The interactions between mesophase-forming copolymers and nanoscopic particles can lead to highly organized hybrid materials. The morphology of such composites depends not only on the characteristics of the copolymers, but also on the features of the nanoparticles. To explore this vast parameter space and predict the mesophases of the hybrids, we develop a mean field theory for mixtures of soft, flexible chains and hard spheres. Applied to diblock/nanoparticle mixtures, the theory predicts new ordered phases,

where particles and diblocks self-assemble into spatially periodic structures. The method can be applied to other copolymer/particle mixtures and used to design novel composite architectures.

(3) Papers Published in Peer-Reviewed Journals

Thompson R, Ginzburg VV, Matsen M, Balazs, AC Predicting the Mesophases of Copolymer/Nanoparticle Composites SCIENCE 292 (5526): 2469-2472 JUNE 29 2001

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Qiu F, Ginzburg VV, Paniconi M, et al. Phase separation under shear of binary mixtures containing hard particles LANGMUIR 15 (15): 4952-4956 JUL 2[illegible] [illegible]99

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Balazs AC, Singh C, Zhulina E Modeling the interactions between polymers and clay surfaces through self-consistent field theory MACROMOLECULES 31 (23): 8370-8381 NOV 17 1998

Lyatskaya Y, Balazs AC Modeling the phase behavior of polymer-clay composites MACROMOLECULES 31 (19): 6676-6680 SEP 22 1998

(4) Participating Personal

Most recently, the project provided postdoctoral training for V.Ginzburg, J. Huh and D. Kuznetsov. Corey Gibbons was an undergraduate who worked on the project and was a co-author on the following paper: Ginzburg VV, Gibbons C, Qiu F, et al. Modeling the dynamic behavior of diblock copolymer/particle composites MACROMOLECULES 33 (16): 6140-6147 AUG 8 2000